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In Situ Oxidation of Y_2O_3 -doped Si_3N_4

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Washington, D.C. 20234

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Interim Report

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Hot-pressed $Si_3N_4+8-13\%Y_2O_3$ compacts, which exhibited catastrophic oxidation in air at $740^\circ C$ but only passive oxidation at $1380^\circ C$, were studied by HVEM using an environmental cell. The *in situ* experiments were started as part of a larger program to establish a model for this catastrophic oxidation process. The low temperatures required for initiation of oxidation are within the capability of the hot stage and the reaction products are sufficiently complex to require analysis by electron diffraction. This yttria-doped silicon nitride ceramic is of interest for use in ceramic turbine engine components because of its good mechanical properties at temperatures above $1200^\circ C$ [1]. However, until the cause of the low temperature catastrophic oxidation is identified and corrected the material cannot be manufactured successfully for these components. The low temperature oxidation is similar in appearance to the so-called "pest condition" and occurs in some billets and not in others which were manufactured under the same apparent commercial, powder processing and hot pressing conditions. Lange *et al.* [2] found that billets they prepared in the $Si_3N_4-Si_2N_2O-Y_2Si_2O_7$ compatibility triangle of the phase equilibrium diagram, shown in Fig. 1, were oxidation resistant; and, that billets with compositions outside this triangle were unstable in oxidizing conditions.

In this paper, the material designated -A- exhibited only passive oxidation during heating in air from $600^\circ C$ to $1400^\circ C$; while the material

designated -B- exhibited catastrophic oxidation during heating in air at 740°C. Both billets* were from the same manufacturer [3] but were purchased at different times. A bar of material -B- when heated in a gradient furnace from 735°C to 1380°C for 20 hours oxidized catastrophically at the low temperature end, and passively at the high temperature end. The major crystalline phases in both materials were identified by powder x-ray diffraction as $\beta\text{Si}_3\text{N}_4$, $\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$ (H phase) and WSi_2 (there were some unidentified lines). The tungsten phase (3-4%) is a result of contamination from WC balls used in ball-milling of the silicon nitride powder, and thus is a common impurity phase in hot-pressed Si_3N_4 . The WSi_2 phase was not present in the catastrophically oxidized portion of the material B, but was present in the portion oxidized at 1380°C. Although the compositions of A and B were similar, there was considerable phase segregation and inhomogeneity in material B as seen in the light microscope. Both materials appear to have compositions outside the compatibility triangle discussed by Lange *et al.* [2].

The Swann environmental cell in the CWRU 650kV electron microscope was used with a platinum strip heater, in flowing oxygen. Specimens of materials -A- and -B- were prepared as ion-thinned discs with one flat side and one dished side. This configuration gave good contact with the grid heater; and, resulted in better heat conduction to the specimen.

The microstructure of the yttria -A- is shown in Fig. 2, and is similar to that found in other billets [4,5]. The large tabular grains are Si_3N_4 , the triangular shaped phases surrounding the grain corners are the $\text{Y}_2\text{O}_3 + \text{Si}_3\text{N}_4$ phases and the dark particles along the grain boundaries are the WSi_2 and/or WC phases. During hot-pressing at 1750-1800°C,

* The specific materials identified are not the only available material.

the yttrium oxynitride phases can melt and form a series of solid solutions with the impurity phases and with the silica in the starting powder [5]. Both crystalline and non-crystalline phases of variable composition can fill the interstices around Si_3N_4 grains.

Specimens were heated gradually to 750°C in 40 torr of O_2 . Under these conditions oxide platelets were seen to nucleate on the surfaces of the $\beta\text{Si}_3\text{N}_4$ grains, around holes and at the yttria phases as in Fig. 3. The platelets, which were randomly oriented and incoherent with the matrix, gave spotty ring patterns both at temperature and after cooling to room temperature. The platelets in Fig. 4 were identified from these ring patterns as a mixture of SiO_2 and $\text{Si}_2\text{N}_2\text{O}$. During the oxidation considerable drift and flexure of the specimens occurred, as is evident in the figures.

After a few minutes of heating, cracks appeared along some grain boundaries; and, as oxidation proceeded a film was observed to grow by the merging of nucleating clusters. These clusters changed diffraction contrast as they merged. It is assumed at this time, that this process represented the gradual reaction and volatilization of the tungsten rich phase. The film thickened and the crack widened to form a sizeable hole as seen in Fig. 5. Iron rich and tungsten depleted phases around reacted thin foil edges were detected with an EDX system on a 200 KV instrument [7].

The yttria-silicon oxynitride phases became porous during the *in situ* oxidation. This type of reaction can be seen at Y in Fig. 5 and in Fig. 6. The morphology of the phases suggests that the initial, yttria-rich regions were multiphase or possibly an amorphous-crystalline mixture. The phase in Fig. 6 was identified from its electron diffraction pattern as YSiO_2N or the K-phase of Fig. 1.

The *in situ* specimens were bent and slightly pink when removed from the strip heaters. Later TEM examination showed that the oxidation had not occurred uniformly over the entire thin area of the specimens. Some of the differences reflect temperature gradient and oxygen partial pressure differences between parts of the specimen that are exposed through holes in the grid heater and other parts of the specimen that were under the grid bars. In the region shown in Fig. 7 few oxide platelets are seen, and the boundaries between Si_3N_4 grains have opened. The yttria phase visible on one edge of the grain was identified as $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$ or the J phase. The oxidation rate differences could reflect also the inhomogeneity of the phase distribution mentioned previously.

Additional *in situ* experiments are needed to verify the mechanism of the loss of W and the observed reaction differences. Video or cine recording will be used to make a more complete record of the observations.

The results of the *in situ* experiments demonstrate that: catastrophic low temperature oxidation in yttria-silicon material -B- started at surfaces exposed to oxygen; volatilization of a W containing phase created voids; continuous films were produced over some grains; yttria rich phases became porous; and considerable strain was associated with the oxidation.

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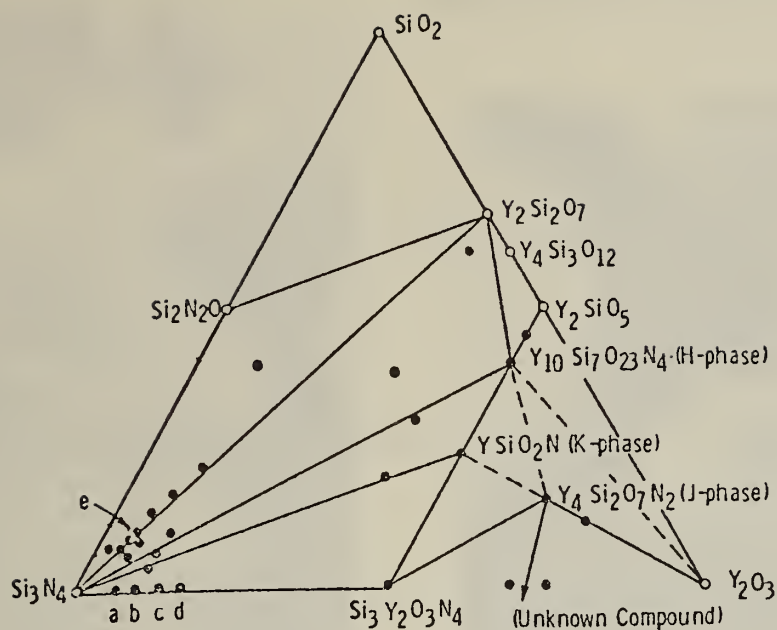


Fig. 1. Phase diagram for the yttria sialons [1].



Fig. 2. Microstructure of hot-pressed $\text{Si}_3\text{N}_4 + 8\%\text{Y}_2\text{O}_3$ showing $\beta\text{Si}_3\text{N}_4$ (β), grains YSiO_2N phase (Y) WSi particles (W).
10 9 2 4



Fig. 3. Material -B- at 750°C in 5200 Pa after heating for ~ 5 min., showing oxide platelets (arrowed) and reacting yttria phase (Y).

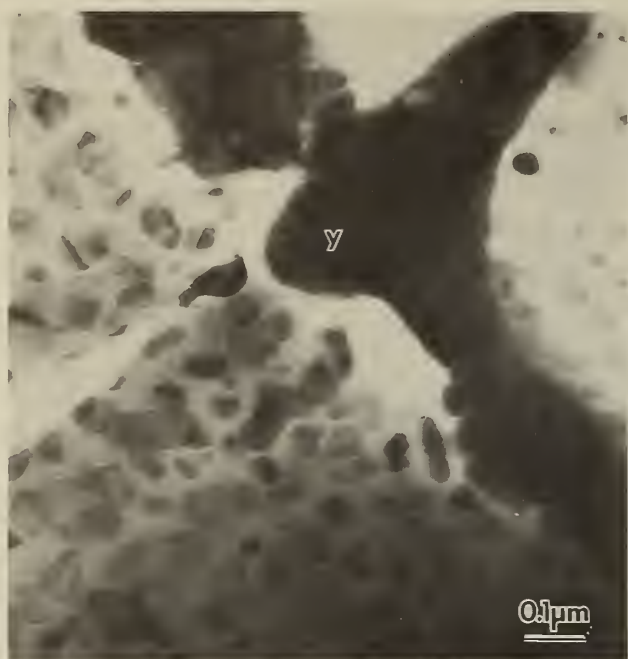


Fig. 4. $\beta\text{Si}_3\text{N}_4$ grain with SiO_2 and Si_2N_2 platelets produced during *in situ* oxidation. Ytttria phase at Y. (Material-B-)



Fig. 5. Specimen at 750°C in 5300 Pa O_2 . The hole (H) and the film around it (Ox) were produced in ~ 30 min (Material-B-).

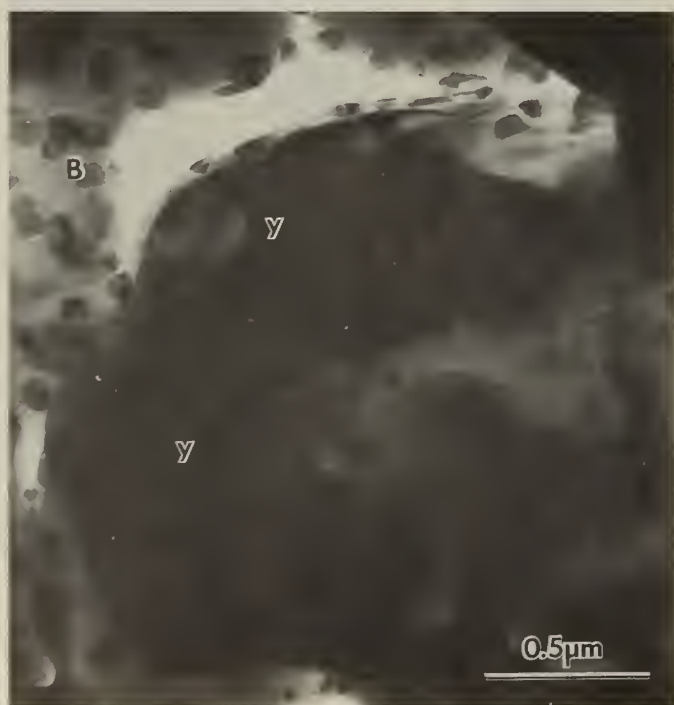


Fig. 6. Material-B-. After oxidation the ytttria phase (Y) is porous and layered, $\beta\text{Si}_3\text{N}_4$ gains (B) have oxide platelets.



Fig. 7. Portion of *in situ* specimen which was under the grid, ytttria phase (Y) is $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$.

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